From Quantum Dynamics to the Second Law of Thermodynamics[1]

Hal Tasaki*

Department of Physics, Gakushuin University, Mejiro, Toshima-ku, Tokyo 171, JAPAN

Abstract

In quantum systems which satisfy the *hypothesis of equal weights for eigenstates* [4], the maximum work principle (for extremely slow and relatively fast operation) is derived by using quantum dynamics alone. This may be a crucial step in establishing a firm connection between macroscopic thermodynamics and microscopic quantum dynamics. For special models introduced in [4, 5], the derivation of the maximum work principle can be executed without introducing any unproved assumptions.

Although there is no doubt that the second law of thermodynamics is one of the most perfect and beautiful laws in physics, its connection to the rest of physics is still poorly understood. It should be stressed that *equilibrium* statistical mechanics does *not* lead to the second law. The second law deals with transformations between two equilibrium states caused by *any* macroscopically realizable processes which can be far from equilibrium. The second law sets sharp and highly nontrivial restrictions on the possibility of such transformations and on the energy exchange during the processes [1].

A traditional approach toward derivation of the second law, which goes back to Boltzmann [2], has been to start from certain stochastic description of microscopic dynamics. In the present note, we wish to concentrate on the possibility of deriving the second law from fully deterministic microscopic quantum dynamics. Such a link between quantum mechanics and thermodynamics (if established) should not only provide a further basis for thermodynamics but also give an indirect support to our belief (which can not been confirmed directly) that even macroscopic systems are governed by quantum mechanics. We shall here concentrate on the second law formulated as the *maximum work principle* (MWP) [3], and describe its derivation in quantum systems which satisfy the conditions stated in [4] for two limiting situations of infinitely slow and relatively (but not infinitely) fast operations. Here we describe only basic ideas of the derivation, and leave details (which are simply technical and not difficult) to [5].

Basic setup and previous results: Let us start by recalling the general ideas and results in [4], where we presented a scenario for deriving the canonical distribution from quantum dynamics, and an example in which such a derivation can be done without making any assumptions. (See [6] for related attempts of deriving statistical physics using quantum dynamics.) We consider an isolated quantum system which consists of a subsystem and a heat bath [7]. The subsystem alone is described by a Hamiltonian H_{S} which is diagonalized as $H_{\mathrm{S}}\Psi_j = \varepsilon_j \Psi_j$ for $j = 1, 2, \ldots, n$, with $\|\Psi_j\| = 1$ and $\varepsilon_j < \varepsilon_{j+1}$. Similarly the bath has a

[1] The first version May 8, 2000.

Hamiltonian $H_{\rm B}$ which is diagonalized as $H_{\rm B}\Gamma_k = B_k\Gamma_k$ for $k = 1, 2, \ldots, N$, with $\|\Gamma_k\| = 1$ and $B_k \le B_{k+1}$. We let $\Omega_{\rm B}(B)$ a smooth function of B such that $\Omega_{\rm B}(B_k) = k$ (*i.e.*, $\Omega_{\rm B}(B)$ is roughly the number of energy levels B_k with $B_k \le B$) and denote by $\rho_{\rm B}(B) = d\Omega_{\rm B}(B)/dB$ the density of states of the bath. Throughout the present note, we only consider a limited range of energy B in which these functions can be approximated as

$$\Omega_{\rm B}(B) \simeq C_1 + C_2 e^{\beta B}, \tag{1}$$

and

$$\rho_{\rm B}(B) \simeq C_3 e^{\beta B}, \tag{2}$$

with constants β, C_1, C_2, and $C_3 = \beta C_2$. Physically speaking, we are assuming that the bath is so large that its inverse temperature β does not vary when it exchanges energy (heat) with the subsystem during equilibration and during operations.

The Hamiltonian for the whole system is

$$H = (H_{\rm S} \otimes \mathbf{1}_{\rm B}) + (\mathbf{1}_{\rm S} \otimes H_{\rm B}) + H_{\rm int}, \tag{3}$$

where $\mathbf{1}_{\rm S}$ and $\mathbf{1}_{\rm B}$ are the identity operators, and $H_{\rm int}$ with $\|H_{\rm int}\| = \lambda$ describes the interaction between the subsystem and the bath [8]. We assume that the bath is macroscopic and the interaction is weak in the sense that

$$\Delta\varepsilon \gg \lambda \gg \Delta B, \tag{4}$$

where $\Delta\varepsilon = \min_j \varepsilon_{j+1} - \varepsilon_j$ and $\Delta B = \max_k B_{k+1} - B_k$ characterize the energy level spacings of the subsystem and the bath, respectively.

For $\ell = 1, \ldots, nN$, let us denote by Φ_ℓ the normalized eigenstate of the total Hamiltonian H with the eigenvalue E_ℓ. We assume that the energy levels are nondegenerate and order them as $E_\ell < E_{\ell+1}$. Let us expand the eigenstate as

$$\Phi_\ell = \sum_{j,k} \varphi^{(\ell)}_{j,k}\, \Psi_j \otimes \Gamma_k. \tag{5}$$

The *hypothesis of equal weights for eigenstates* proposed in [4] is that, for a *general* interaction, the above coefficients $\varphi^{(\ell)}_{j,k}$ satisfy

$$|\varphi^{(\ell)}_{j,k}|^2 \sim f(E - (\varepsilon_j + B_k)), \tag{6}$$

for *general* ℓ with E_ℓ in a certain range [9], where the function $f(x)$ has a single peak at $x = 0$ and is negligible for $|x| \ge C_4\lambda$, where C_4 is a constant. The hypothesis looks natural since, when $\lambda = 0$, only (j, k) such that $E - (\varepsilon_j + B_k) = 0$ contribute to the expansion (5). In [4], we presented an artificial example in which this hypothesis can be established rigorously without any assumptions. See [5] for a further (simpler) example.

Once accepting (6), it is easily observed that [4, 5], for any operator A of the subsystem,

$$\begin{aligned}\langle\Phi_\ell,(A\otimes\mathbf{1}_{\rm B})\Phi_\ell\rangle &\simeq \sum_{j,k}(A)_{j,j}|\varphi^{(\ell)}_{j,k}|^2\\ &\simeq \frac{\sum_j (A)_{j,j}\,\rho_{\rm B}(E_\ell-\varepsilon_j)}{\sum_j \rho_{\rm B}(E_\ell-\varepsilon_j)} \simeq \langle A\rangle^{\rm canonical}_\beta,\end{aligned} \tag{7}$$

where the final estimate follows from (2). Here $\langle\cdots\rangle^{\rm canonical}_\beta$ denotes the canonical expectation at inverse temperature β. Furthermore it can be shown that for any initial state

$$\Phi(0)=\sum_\ell \gamma_\ell\,\Phi_\ell, \tag{8}$$

with coefficients γ_ℓ almost identically distributed for ℓ such that $|E_\ell-\bar{E}|\le\delta$, for some $\bar{E}$ and a constant δ satisfying $\Delta B\ll\delta\ll\Delta\varepsilon$, one has

$$\langle\Phi(t),(A\otimes\mathbf{1}_{\rm B})\Phi(t)\rangle\simeq\langle A\rangle^{\rm canonical}_\beta, \tag{9}$$

for sufficiently large and typical t, where $\Phi(t)=e^{-iHt}\Phi(0)$ is the state at time t. We have therefore shown (under the hypothesis about the structure of eigenstates) that quantum dynamics alone brings the system into the canonical distribution.

External operation and work: We wish to treat a situation typical in thermodynamics, where an external agent performs an operation to the subsystem (e,g, moving a piston attached to a cylinder) leaving the bath untouched . We model the operation as a change of the Hamiltonian of the subsystem. More precisely, the Hamiltonian for the subsystem is $H_{\rm S}(t)$ with $H_{\rm S}(t)=H_{\rm S}$ for $t\le t_0$ and $H_{\rm S}(t)=H'_{\rm S}$ for $t\ge t_0+\tau$. The operation takes place between t_0 and $t_0+\tau$, and the Hamiltonian is constant otherwise. We denote by $\varepsilon'_{j'}$ the eigenvalues of $H'_{\rm S}$.

Let $\Phi(0)$ be the initial state as in (8), and let $\Phi(t)$ be its time evolution determined by the time-dependent Hamiltonian $H(t)=(H_{\rm S}(t)\otimes\mathbf{1}_{\rm B})+(\mathbf{1}_{\rm S}\otimes H_{\rm B})+H_{\rm int}$. We assume that t_0 is chosen sufficiently large so that $\Phi(t_0)$, which is the state right before the operation, describes the thermal equilibrium in the sense of (9). When t becomes sufficiently large, the state $\Phi(t)$ is expected to reach the new equilibrium after the operation [10].

From the energy conservation law, one finds that the work done by the subsystem to the external agent [11] is

$$W=\langle\Phi(t_0),H\,\Phi(t_0)\rangle-\langle\Phi(t_0+\tau),H'\,\Phi(t_0+\tau)\rangle, \tag{10}$$

where H' denotes the total Hamiltonian for $t\ge t_0+\tau$. The *maximum work principle* (MWP) states that the above work satisfies the inequality

$$W\le F(\beta)-F'(\beta), \tag{11}$$

for any operations, and the equality holds if the operation is done infinitely slowly. Here $F(\beta)=-\beta^{-1}\log\sum_j e^{-\beta\varepsilon_j}$ and $F'(\beta)=-\beta^{-1}\log\sum_j e^{-\beta\varepsilon'_j}$ are the free energies of the subsystem before and after the operation, respectively.

Slow operation: We first consider infinitely slow operation realized in the $\tau \to \infty$ limit, which corresponds to quasi-static operations in thermodynamics. In this limit, time evolution of the state $\Phi(t)$ is completely determined by the adiabatic theorem in quantum mechanics [12] if we assume that the Hamiltonian $H(t)$ has no degenerate eigenstates for any t. If one starts from one of the eigenstates of H, the time evolution of the state exactly traces the corresponding eigenstate of $H(t)$ during the operation. Thus if we start from $\Phi(0)$ of the form (8), the state right after the operation is written as $\Phi(t_0+\tau) = \sum_\ell \gamma_\ell\, \theta_\ell\, \Phi'_\ell$, with $|\theta_\ell| = 1$. Here Φ'_ℓ is the eigenstate of H' with the eigenvalue E'_ℓ, where the energy levels are again ordered as $E'_\ell < E'_{\ell+1}$.

In order to estimate the work done by the subsystem, we introduce the index $\bar{\ell}$ such that $E_{\bar{\ell}} = \bar{E}$, where $\bar{E}$ is (roughly) the mean energy of the state $\Phi(t)$ before the operation. The mean energy after the operations is simply given by $\bar{E}'_{\rm slow} = E'_{\bar{\ell}}$. Therefore the energies $\bar{E}$ and $\bar{E}'_{\rm slow}$ are related by

$$\Omega(H \le \bar{E}) = \Omega(H' \le \bar{E}'_{\rm slow}), \tag{12}$$

where $\Omega(A \le a)$ denotes the number of eigenstates of a hermitian matrix A with eigenvalues less than or equal to a [13].

Since $\|H_{\rm int}\| = \lambda$, we can neglect $H_{\rm int}$ in (12) to get

$$\Omega(H_{\rm S} + H_{\rm B} \le \bar{E}) \simeq \Omega(H'_{\rm S} + H_{\rm B} \le \bar{E}'_{\rm slow}), \tag{13}$$

with errors of $O(\lambda)$ in the energies [14]. By treating the energy levels of $H_{\rm S}$ and $H'_{\rm S}$ explicitly, we can rewrite (13) as

$$\sum_{j=1}^{n} \Omega_{\rm B}(\bar{E} - \varepsilon_j) \simeq \sum_{j=1}^{n} \Omega_{\rm B}(\bar{E}'_{\rm slow} - \varepsilon'_j). \tag{14}$$

By using (1), the relation (14) immediately implies

$$W_{\rm slow} \equiv \bar{E} - \bar{E}'_{\rm slow} \simeq F(\beta) - F'(\beta), \tag{15}$$

which is the equality corresponding to the desired MWP (11).

Fast operation: Next we consider the opposite situation where the operation is executed quickly. We assume that the duration of the operation satisfies $\tau \ll \lambda^{-1}$. In other words, the operation is done so quickly that the subsystem and the bath essentially do not exchange energy (heat) during the operation. The exchange of heat takes place in the equilibration process after the operation.

Since we have chosen t_0 so that $\Phi(t_0)$ describes the equilibrium, it can be expanded as

$$\Phi(t_0) = \sum_{j,k} \xi_{j,k} \Psi_j \otimes \Gamma_k, \tag{16}$$

where the coefficients $\xi_{j,k}$ satisfy the hypothesis of equal weight (6) just as $\varphi^{(\ell)}_{j,k}$.

Let us consider the time evolution during the operation. From the assumption of quick operation, the state of the bath essentially remains unchanged while that of the subsystem

changes according to a unitary transformation $\Psi_j \to \sum_{j'} U_{jj'}\Psi'_j$. Here we diagonalized $H'_{\rm S}$ as $H'_{\rm S}\Psi'_j = \varepsilon'_j\Psi'_j$ with $\varepsilon'_j < \varepsilon'_{j+1}$.

Then the state immediately after the operation is

$$\Phi(t_0+\tau) \simeq \sum_{j,j',k} \xi_{j,k} U_{jj'}\Psi_{j'} \otimes \Gamma_k. \tag{17}$$

We can evaluate the energy expectation value of this state as in (7) to get

$$\begin{aligned}
&\bar{E}'_{\rm fast} \equiv \langle \Phi(t_0+\tau), H'\,\Phi(t_0+\tau)\rangle \\
&= \sum_{j',k} |\sum_j \xi_{j,k} U_{jj'}|^2 2(B_k + \varepsilon'_{j'} + O(\lambda)) \\
&\simeq \frac{\sum_{j,j'} \rho_{\rm B}(\bar{E}-\varepsilon_j)|U_{jj'}|^2(\bar{E}-\varepsilon_j+\varepsilon'_{j'})}{\sum_j \rho_{\rm B}(\bar{E}-\varepsilon_j)} \\
&\geq \frac{\sum_j \rho_{\rm B}(\bar{E}-\varepsilon_j)(\bar{E}-\varepsilon_j+\varepsilon'_j)}{\sum_j \rho_{\rm B}(\bar{E}-\varepsilon_j)},
\end{aligned} \tag{18}$$

where we used (6) to get the third line. The final inequality follows [15] by noting that $\varepsilon'_{j'}$ is increasing in j' while $\rho_{\rm B}(\bar{E}-\varepsilon_j)$ is decreasing in j, and $\sum_j |U_{jj'}|^2 = \sum_{j'} |U_{jj'}|^2 = 1$. On the other hand, sine $\Omega_{\rm B}(B)$ is convex in B, (14) implies that

$$\begin{aligned}
&\sum_{j=1}^n \Omega_{\rm B}(\bar{E}-\varepsilon_j) \simeq \sum_{j=1}^n \Omega_{\rm B}(\bar{E}'_{\rm slow}-\varepsilon'_j) \\
&= \sum_{j=1}^n \Omega_{\rm B}(\bar{E}-\varepsilon_j + (\bar{E}'_{\rm slow}-\bar{E}-\varepsilon'_j+\varepsilon_j)) \\
&\geq \sum_{j=1}^n \Omega_{\rm B}(\bar{E}-\varepsilon_j) + \sum_{j=1}^n (\bar{E}'_{\rm slow}-\bar{E}-\varepsilon'_j+\varepsilon_j)\rho_{\rm B}(\bar{E}-\varepsilon_j),
\end{aligned} \tag{19}$$

and hence

$$\bar{E}'_{\rm slow} \lesssim \frac{\sum_j \rho_{\rm B}(\bar{E}-\varepsilon_j)(\bar{E}-\varepsilon_j+\varepsilon'_j)}{\sum_j \rho_{\rm B}(\bar{E}-\varepsilon_j)}. \tag{20}$$

Then from (18), we find $\bar{E}'_{\rm slow} \lesssim \bar{E}'_{\rm fast}$ [16], and by recalling (15), we find

$$W_{\rm fast} \equiv \bar{E} - \bar{E}'_{\rm fast} \lesssim W_{\rm slow} \simeq F(\beta) - F'(\beta), \tag{21}$$

which is the desired MWP.

Discussions: We have derived the MWP for infinitely slow and relatively (but not infinitely) fast operations by using quantum dynamics and our *hypothesis of equal weights for eigenstates*. Note that since the hypothesis has been proved for some models [4, 5], we now have derived rigorously the (parts of the) second law of thermodynamics in concrete quantum mechanical models [17]. As we have discussed in [4, 5], we believe that our hypothesis is valid in a rather general class of quantum systems.

Among many questions to be discussed, let us address two particularly important ones. The first natural question is whether the MWP can be derived for general operations which are neither extremely slow nor very quick. A naive perturbative estimate around the $\tau \to \infty$ limit suggests the validity of the MWP, but to construct rigorous estimate from such a heuristic calculation seems quite difficult. A rigorous analysis of general operations seems formidably difficult since we have almost no ways of treating general time evolution in quantum systems with time dependent Hamiltonians. Moreover although unquestionable success of thermodynamics may seem to suggest the universal validity of the MWP, one should note that in experiments one only encounters operations which are realized as motions of macroscopic objects. There is a possibility that a very carefully designed time-dependent Hamiltonian $H_{\rm S}(t)$ leads to a time evolution which violates the MWP. If this is the case, all that we can hope to prove is the validity of the MWP for a limited class of operations which are "macroscopically realizable." For the moment, we have no idea about what criteria should we use to distinguish such operations.

The second question is whether our result applies to realistic situations where one applies many operations repeatedly to the subsystem. To answer this, suppose that we start from an initial state (8) where γ_ℓ is nonvanishing only for ℓ such that $|\bar{E} - E_\ell| \le \delta$. After a general operation, we end up with a similar state, but with a different mean energy $\bar{E}'$ and the energy range δ' which is in general strictly larger than than the initial δ. Therefore if we repeat general operations sufficiently many times, the range δ becomes large and may violate the required condition $\delta \ll \Delta\varepsilon$. Therefore, technically speaking, although we *can* use the present result as long as the number of operations does not exceed a certain limit (which limit depends on the initial state and the nature of the operations), there is no hope of dealing with indefinitely many operations. We still do not know if this limitation contradicts with our experiences that the second law of thermodynamics has been confirmed in repeated experiments [18].

It is a pleasure to thank Tohru Koma, Yoshi Oono, and Shin-ichi Sasa for stimulating discussions on various related topics.

References

[*] Electronic address: hal.tasaki@gakushuin.ac.jp

[1] The content of the second law is explained in almost any textbooks of thermodynamics. For a recent clear and logical formulation, see E. H. Lieb and J. Yngvason, Phys. Rep. **310**, 1 (1999).

[2] L. Boltzmann, Wiener Berichte **53**, 195 (1866).

[3] Recently Jarzynski [Phys. Rev. Lett. **78**, 2690 (1997)] proved the MWP for a classical dynamical system with an initial condition sampled from the canonical distribution. For a related result in Langevin thermodynamics, see K. Sekimoto and S. Sasa, J. Phys.

Soc. Jpn., **66**, 3326 (1997). See also S. Sasa and S. Komatsu, Prog. Theor. Phys. **103**, 1 (2000) (cond-mat/9911181).

[4] H. Tasaki, Phys. Rev. Lett. **80**, 1373 (1998).

[5] H. Tasaki, to be published.

[6] R. V. Jensen and R. Shanker, Phys. Rev. Lett. **54**, 1879 (1985); K. Saito, S. Takesue and S. Miyashita, J. Phys. Soc. Jpn. **65**, 1243 (1996), Phys. Rev. E **54**, 2404 (1996); M. Srednick, Phys. Rev. E **50**, 888 (1994), J. Phys. A **29** L75 (1996); G. Casati (cond-mat/9801063).

[7] One can also try recovering thermodynamics (in the (U, X)-representation as in [1]) from a single isolated quantum system. We feel, however, that an approach using the bath and the subsystem is less involved both conceptually and technically.

[8] $\|A\|$ denotes the maximum of the absolute values of the eigenvalues of a hermitian matrix A.

[9] Of course it is a highly debatable question to decide which quantum systems and which quantum states are "general."

[10] As in [4], we here concentrate on the situation where $\Phi(t)$ is a pure state, but to treat mixed states is a trivial extension.

[11] We are implicitly assuming that the external agent is "classical", and the difference W between the two quantum mechanical expectation values can be regarded as the classical work.

[12] Note that the word "adiabatic" is used here to indicate very slow change of parameters (while its primary meaning in thermodynamics is "without heat exchange"). For our purpose the classical adiabatic theorem proved by Born and Fock [Z. Phys. **5**, 165 (1928)] suffices. For modern extensions, see G. Nenciu, Commun. Math. Phys. **152**, 479 (1993), and references therein.

[13] For a (pure) state of the whole system whose energy is concentrated at $\bar{E}$, we can define its Boltzmann entropy by $S = k \log \Omega(H \le \bar{E})$. Then (12) states that the entropy of a closed system remains unchanged during a slow operation, and this is true for an arbitrary slow operation on the whole system. Such an implication of the adiabatic theorem has been of course wellknown.

[14] More precisely it is well known [5] that Weyl's minimax principle implies the bounds $\Omega(H_0 \le \bar{E} - \lambda) \le \Omega(H \le \bar{E}) \le \Omega(H_0 \le \bar{E} + \lambda)$ (and the corresponding bounds for H'), where $H_0 = H - H_{\rm int}$. Throughout the present note, approximate equalities ($\simeq$) and inequalities ($\lesssim$) should be regarded as rigorous equalities and inequalities, respectively, but with small errors of $O(\lambda)$ or $O(\delta)$.

[15] Let f_i, g_i be nondecreasing in i, and $\alpha_{ij} \geq 0$ satisfy $\sum_i \alpha_{ij} = \sum_j \alpha_{ij} = 1$. Then by expanding the left-hand side of the trivial inequality $\sum_{i,j}(f_i - f_j)\alpha_{ij}(g_i - g_j) \geq 0$ one gets $\sum_{i,j} f_i \alpha_{ij} g_j \leq \sum_i f_i g_i$.

[16] As in [13], this implies the corresponding inequality $S \leq S'$ for the Boltzmann entropy for the whole closed system. Unlike the corresponding equality [13], however, the same inequality for *arbitrary* fast (or instantaneous) operations on the whole system is not valid. (One can easily write down counterexamples.) We expect the inequality to be valid for generic macroscopic operations.

[17] To prove (15) rigorously in the model of [4], we have to let H_{int} depend on t.

[18] One may argue that, in reality, the initial energy range δ happened to be extraordinarily small, and realistic operations (which are not too fast) do not increase the range δ too much. One may also argue, however, that we are not allowed to rely on initial condition too much, and must consider some mechanisms (like "decoherence"?) which "refreshes" quantum states by narrowing the range δ.